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Automatic Recording of Liquid Penetration through Filter Paper and Wetting Behavior of Liquids

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The penetration of liquid through a vertically suspended filter paper was studied by measuring the weight increase with a strain gauge tensiometer for several organic liquids and aqueous solutions. The plot of penetration rate $K=h/t^{1/2}$ (h, height of liquid rise and t, time) against $(\sigma/\eta)^{1/2}$ (σ, surface tension and η, viscosity coefficient of wetting liquids) showed two straight lines, one for organic liquids and the other for aqueous solutions of sodium dodecyl sulfate. Both these lines passed the origin, suggesting Lucas-Washburn formula to hold. The plots for ethyl alcohol–water mixtures showed behaviors intermediate between those two linear relations. The aqueous solutions caused swelling of fibers and reduced the mean capillary radius of the filter paper, resulting in a decrease of the penetration constant $P=K/(\sigma/\eta)^{1/2}$ but with a rather large K value. The plots for penetration of water through an untreated paper fell far below the straight line obtained for aqueous solutions of sodium dodecyl sulfate. The penetration was recovered by removing fatty contaminants from the filter paper using Soxhlet extractor with ether. The results of a simple test of unfolding a folded paper by touching it with liquids are also in line with those mentioned above.

A number of studies have since been made for the wetting of the fibrous and powder materials as a function of the porosity of fiber,[1-3] the degree of dispersion of powder, the surface treatment and the effect of surface-active agent[4] on these substances. The sinking time of solid sample may be used as a simple criterion of

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[1] R. Lucas, *Kolloid-Z.*, **21**, 105 (1917). E. W. Washburn, *Phys. Rev. Ser.* 2, **17**, 273 (1921).

[2] P. L. Peek and D. A. McLean, *Ind. Eng. Chem. Anal. Ed.*, 85 (1934).

[3] Z. E. Wolkowa, *Kolloid-Z.*, **67**, 280 (1934); J. M. Dallavalle, "Micromeritics," Second edition, Pitman Publishing Corporation, New York, London (1952).

[4] A. M. Schwartz and J. W. Perry, "Surface Active Agent," Vol. 1, Interscience Publisher, New York (1957).

wetting power of surface-active agent,[5] while wettabilities of fibers,[6,7] filter papers[8,9] and powder materials[10,11] are measured by the penetration velocity or pressure of a liquid through the sample strip or the powders packed in a column. The rate of penetration should be a subject worth studying from both theoretical and practical interest. However, the frontal line of the ascending liquid is not easy to find visually because of its irregular and rapid movement, sepecially at the initial stage of penetration. This difficulty has been overcome by measuring the changes of the weight or the electrical capacity of the sample due to the liquid penetration, by torsion balance[6] or capacity meter.[11] In the present study, the weight increase was measured by a self-recording strain gauge tensiometer[12] which enabled a simple and accurate measurement of the kinetic process of penetration, especially at its early stage.

The penetration of filter paper by various liquids and solutions is described in the present paper to elucidate the different wetting and swelling behaviors of the filter paper towards water and organic liquids. Of the numerous studies of a similar nature[8] only little has been reported on these behaviors.[9]

Experimental

Materials. Ethyl alcohol, butyl alcohol, acetone, dioxane, *n*-hexane, and toluene were purified by dehydration and distillation.[13] Sodium dodecyl sulfate (SDS) was prepared by the sulfation of dodecyl alcohol free from its homologues, and was used after repeated purification.[14] Water used was obtained by refluxing ordinary distilled water first with acid permanganate, then distilling from alkaline permanganate solution, and finally distlling twice with a Hysil flask. The filter paper (No. 50 for chromatography, Toyo Filter Paper Co., Japan) was cut into strips 2×7 cm so as to make its total weight after the penetration within the maximum permissible load (300 mg) of the strain gauge. The paper was subjected to extraction with ether to remove fatty contaminants.

Apparatus and Measurement. A cantilever type self-recording strain gauge tensiometer[12] (Fig. 1) was used for the measurement of liquid penetration. A strip of filter paper was hung from the end of the tension arm, and the wetting liquid was introduced from the reservoir into the cell until it just touched the lower end of the filter paper. An increase of weight of the filter paper due to the penetration of liquid was converted into an electrical output by the strain gauge, and recorded with a 1 mV full scale recorder (QPD 33, Hitachi, Japan). The apparatus was kept at 30°C in a thermostat designed so as to keep the cell from outer environment and prevent the evaporation of solutions.[15] The reading of the recorder was calibrated to the height H of penetrating liquid from the electrical output of tensiometer for the liquid rise of unit length. The measurement was started after the saturation of the cell with the vapor of sample liquid. About five minutes of measurement was enough for analysis, since the approximate Eq. (2) was used which is only applicable for the early stage of penetration. A slight change of the surface tension with time and of the depth of paper in a liquid, caused a negligible error in the calculation of H. The viscosity of liquid was measured by an Ostwald viscometer, and the surface tension of liquid was measured by the same tensiometer using Wilhelmy's glass plate.[12] All measurements were made at 30°C.

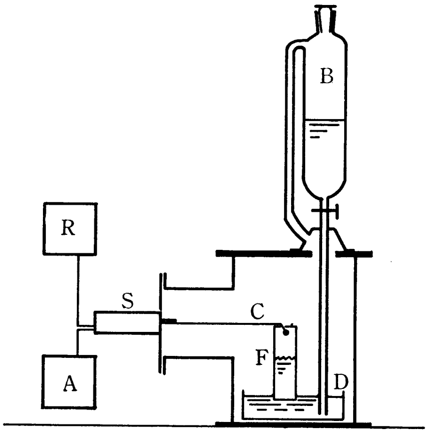

Fig. 1. Strain gauge tensiometer for penetration measurement.

A: DC Supply
B: Reservoir
C: Tension arm
D: Sample solution
F: Filter paper
R: Recorder
S: Strain gauge

Results and Discussion

The velocity of liquid ascending through fibrous material like filter paper was given by Peek and McLean[2] as

$$\mathrm{d}h/\mathrm{d}t = \bar{r}\sigma\cos\theta/4h\eta - \bar{r}^2 dg/8\eta \qquad (1)$$

where h denotes the height of liquid at time t, $\bar{r}$ the mean capillary radius, σ the surface tension, η the viscosity coefficient, d the density, g the gravity constant and θ the contact angle. At the initial stage of penetration Eq. (1) is approximated by

$$\mathrm{d}h/\mathrm{d}t = \bar{r}\sigma\cos\theta/4h\eta \qquad (2)$$

which, after integration, gives Lucas-Washburn formula[1]

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[5] J. L. Moilliet and Collie, "Surface Activity," E. & F. N. Spon Ltd., London (1951), F. M. Fowkes, *J. Phys. Chem.*, **57**, 98 (1953); T. Hikota, K. Morohara, and K. Megro, This Bulletin, **43**, 3913 (1970); W. Yano, S. Takeo, and W. Kimura, *Yukagaku*, **11**, 241 (1962).

[6] H. Sand, *Kolloid-Z.*, **183**, 57 (1961).

[7] H. Sanuki, K. Kuri, and K. Ota, *Sen-i Gakkaishi*, **21**, 91 (1965); H. Sanuki, K. Ito, and K. Ota, *ibid.*, **21**, 506 (1965).

[8] H. Fujita, *J. Phys. Chem.*, **56**, 625 (1952); T. Gillespie, *J. Colloid Sci.*, **13**, 32 (1958); M. Nakagaki and Osagawa, This Bulletin, **32**, 344 (1958); T. Gillespie, *J. Colloid Sci.*, **14**, 123 (1959); J. Szekely, A. W. Newmann, and Y. K. Chung, *ibid.*, **35**, 273 (1971); T. Kuwamura, E. Takahashi, and M. Oshima, *Yukagaku* **21**, 100 (1972).

[9] T. Gillespie and T. Johnson, *J. Colloid Sci.*, **36**, 282 (1971).

[10] F. E. Bartell and H. Y. Jenings, *J. Phys. Chem.*, **38**, 495 (1934).

[11] M. Wada and N. Miyamoto, *Res. Inst. Dress. Met.*, **15**, 41 (1959). M. Wada and T. Yamamoto, *ibid.*, **21**, 53 (1965).

[12] M. Koshinuma, A. Nakamura, T. Seimiya, and T. Sasaki, This Bulletin, **45**, 344 (1972).

[13] A. Weissberger and E. S. Proskauer, "Technique of Organic Chemistry," Vol. 7, ed. by A. Weissberger, Interscience Publisher, New York, London (1955), pp. 318—379.

[14] E. E. Dreger, *Ind. Eng. Chem.*, **36**, 610 (1944).

[15] T. Seimiya and T. Sasaki, *J. Colloid Interfac. Sci.*, **21**, 229 (1966).

$$h = (\bar{r}\sigma\cos\theta/2\eta)^{1/2}t^{1/2} = Kt^{1/2} \qquad (3)$$

Thus a plot of h *vs.* $t^{1/2}$ should give a straight line with a slope K, which is called hereafter the rate of penetration of liquid. If $\bar{r}$ is known, wetting tension $\sigma\cos\theta$ can be calculated from Eq. (3). We see also that in the case of constant $\bar{r}\cos\theta$, plot of K *vs.* $(\sigma/\eta)^{1/2}$ for various liquids should lie on the same straight line passing through the origin with a slope $P=(\bar{r}\cos\theta/2)^{1/2}$, which is called hereafter the penetration constant.

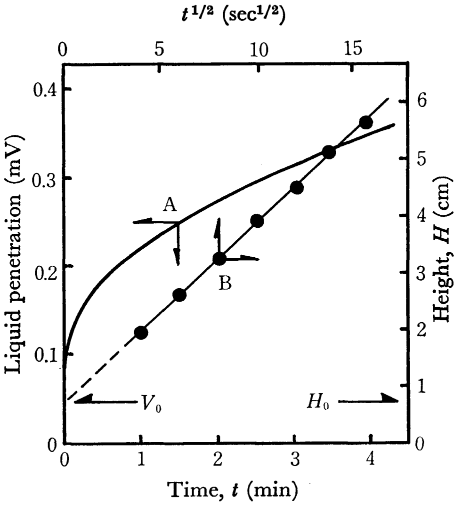

Fig. 2. Typical example of output against time and height against $t^{1/2}$ for water penetration.

Curve A in Fig. 2 shows a typical example of the liquid penetration process. The recorder reading increases along a parabolic curve with time, after an abrupt increase V_0, due to the pull by surface tension of liquid. The reading in terms of the apparent liquid rise H is plotted against $t^{1/2}$ as shown by the straight line B in Fig. 2. The value of H_0 (corresponding to V_0) was obtained by extrapolation as shown in the figure. Since $h=H-H_0$ is the true height of liquid rise, the straight line B with H_0 as zero point is taken as the h *vs.* $t^{1/2}$ plot. The linear relations are seen to hold for all systems so far studied, and show the Lucas-Washburn formula to hlod at least for the initial several minutes of the penetration process. Some typical results are shown in Fig. 3. The fair agreement with Lucas-Washburn formula might also imply the constancy of surface tension, presumably a dynamic one,[6,16] and the absence of chromatographic separation of solute at the ascending front in its initial stage. In the case of aqueous SDS solution, extrapolation to time zero was necessary to obtain the dynamic surface tension.

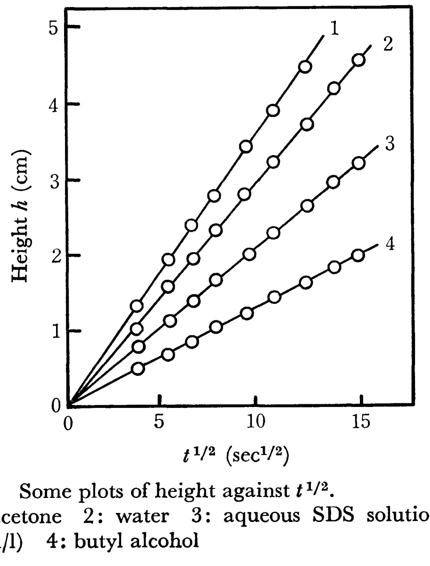

Fig. 3. Some plots of height against $t^{1/2}$.
1: acetone 2: water 3: aqueous SDS solution 1×10^{-2} (mol/l) 4: butyl alcohol

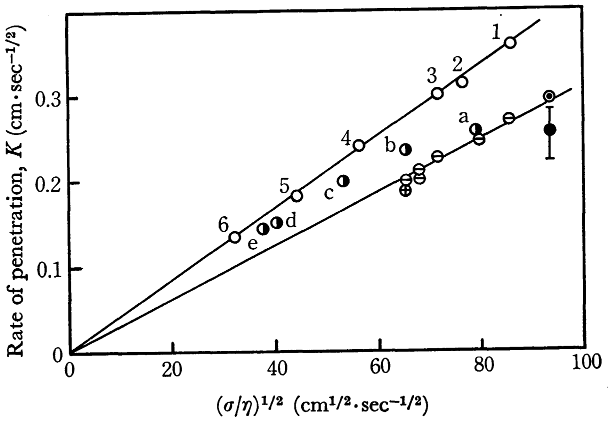

Fig. 4. Plots of rate of penetration against $(\sigma/\eta)^{1/2}$.
○: organic liquids, 1: acetone 2: *n*-hexane 3: toluene 4: dioxane 5: ethyl alcohol 6: butyl alcohol
◑: aqueous ethyl alcohol solutions (vol %), a: 5% b: 10% c: 20% d: 40% e: 60%
⊙: water, ●: water (untreated filter paper)
⊖: aqueous SDS solutions, ⊕: aqueous SDS solutions (untreated filter paper)

The plots of K *vs.* $(\sigma/\eta)^{1/2}$ are shown in Fig. 4. As expected, all plots for organic liquids tested fell on the same straight line passing through the origin with a slope $P=(\bar{r}\cos\theta/2)^{1/2}=4.3\times10^{-3}$ cm$^{1/2}$. Since $\bar{r}$ is considered to be constant for a given filter paper, the constancy of $\bar{r}\cos\theta$ means the constant θ, presumably zero degree, because most organic liquids are known to show zero contact angle against various compact solid surfaces.[2] The fact that Soxhlet extraction of the filter paper was immaterial for the penetration by organic liquids is quite reasonable, since the contact angles are unaffected by contamination and remain zero for these liquids. Figure 4 shows also that the plots for water and aqueous solutions considerably fall off the linear relation for the organic liquids. In the case of water penetration, removal of fatty contamination from the filter paper was seen to cause a remarkable increase of K value. The fact that the wetting of filter paper by aqueous SDS solution or organic liquids was not affected by the removal of fatty contamination of the paper also confirms this view. However, the increase of K due to the removal of contamination still does not bring the plots on the line obtained for the organic liquids. This can not be due to the incomplete removal of the contamination, since even a good wetting SDS solution can not bring the plots on the line of the organic liquids. This might suggest that the contact angle has already attained zero value, and that the decrease of $\bar{r}$ due to the swelling of fiber, for instance, affects the penetration by water or aqueous solutions.

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[16] H. Lange, *Kolloid-Z.*, **136**, 136 (1954).

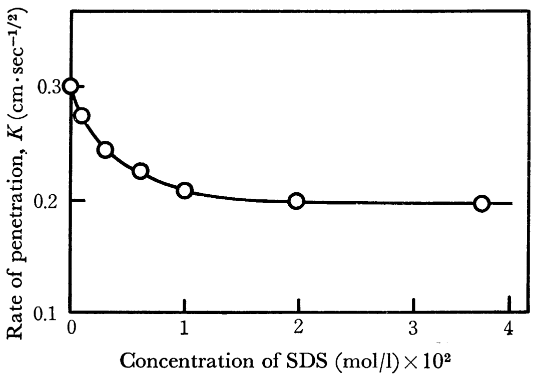

Fig. 5. Concentration dependence of rate of penetration K for aqueous SDS solutions.

The plots for aqueous SDS solutions and pure water lie on a straight line of smaller P than that for organic liquids. This may mean that the value of $\bar{r}$ for these aqueous systems is constant and smaller than that for organic liquids. The values of $\bar{r}$ estimated from the slope of straight lines in Fig. 4 are 3.4×10^{-5} cm for organic liquids, and 2.0×10^{-5} cm for both water and aqueous SDS solutions. The contact angle between pure water and the untreated filter paper is found to be 43°. The change of K with the concentration of SDS for clean filter paper is also shown in Fig. 5. The value of K decreased with increasing SDS concentration in contrast with the increased wetting of fibrous material contaminated with fatty substances.[14)]

The penetration experiment of the filter paper by ethyl alcohol–water mixtures of various compositions revealed that the various states of swelling probably depend on the concentratration of ethyl alcohol. As seen in Fig. 4, the plots moved from the linear relation for aqueous solutions to that for organic liquids as the alcohol content increased. This may be caused by the increase of $\bar{r}$ with the decrease of water content and accordingly the decrease of the swelling. Curve A in Fig. 6 shows the regular increase of the P value with the concentration of ethyl alcohol in water, while the K value shows an irregular change with the alcohol concentration. Thus P is reasonably used as a measure of penetration.

As a simple demonstration of swelling, the rate of unfolding of a folded paper strip was measured by applying a drop of liquid on the folded part of the paper (Fig. 7). No unfolding was observed for organic liquids tested, but for water and aqueous SDS solutions, it was full and instantaneous. The difference in unfolding also explains the difference in penetration shown by two straight lines in Fig. 4. Although the rate of penetration K is larger for n-hexane and acetone than that for water, the organic liquids neither cause swelling nor unfolding. The time for half-unfolding of the paper by aqueous solution of ethyl alcohol is also shown as curve B in Fig. 6. Unfolding and swelling were seen to be instantaneous in water-rich solutions. Half-unfolding angle of 90° was never reached at a concentration of ethyl alcohol higher than 80%. The tendency of non-unfolding presumed from a saturation of P value at higher concentration of ethyl alcohol seen in curve A of Fig. 6, is in line with the increasing tendency of unfolding time.

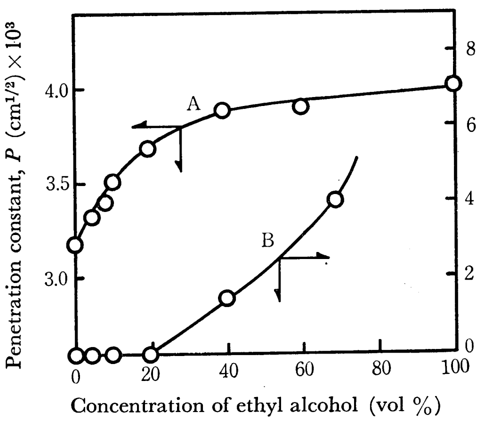

Fig. 6. Plots of penetration constant P and time of half unfolding against ethyl alcohol concentration.

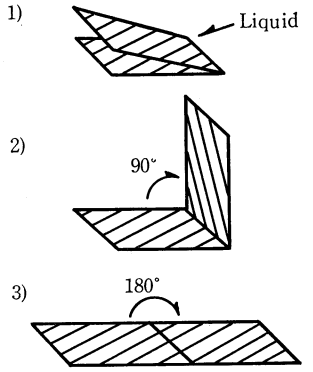

Fig. 7. Unfolding of filter paper strips.
1): no unfolding 2): half unfolding 3): full unfolding

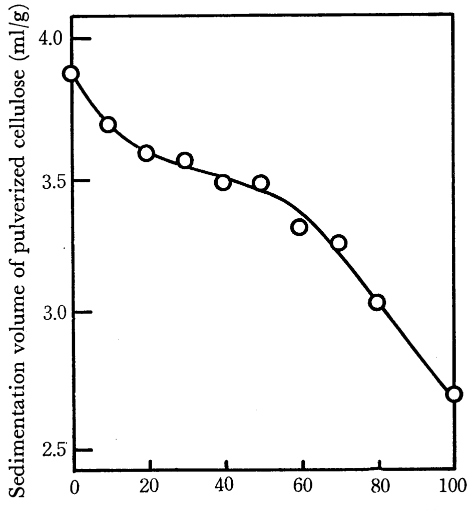

Fig. 8. Sedimentation volumes of *Avicel* in aqueous ethyl alcohol solutions.

The measurement of the sedimentation volume of pulverized cellulose in aqueous ethyl alcohol solution was carried out. The result shows that the tendencies of both swelling and non-swelling of cellulose depend on the concentration of ethyl alcohol. Figure 8 shows a decrease of sedimentation volume of pulverized cellulose (Avicel, Asahi Chemicals Inc., Japan) with increase of concentration of ethyl alcohol. This might also support the above view.